PHYSICAL CHARACTERISTICS OF OSMOTIC MEMBRANES OF ORGANIC POLYMERS

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
August, 1957

ACKNOWLEDGMENTS

The research described in this dissertation was supported by the Office of Saline Water, U. S. Department of the Interior.

Calvin J. Workinger, Ernest J. Breton, Jr., Charles E. Reid, and Gordon M. Smith collaborated in the design and construction of apparatus.

I should like to express my appreciation for the guidance given me by the supervisory committee, and in particular, to my faculty advisor, Charles E. Reid.

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INTRODUCTION

The use of synthetic osmotic membranes for desalting saline waters was proposed by Reid (1) in 1953. This process involves reversal of osmotic flow from a solvent cell to a solution cell across a semipermeable membrane. Pressure, more than sufficient to counterbalance the osmotic pressure of the solution, applied to the solution cell will reverse the direction of flow. The feasibility of the process depends upon the discovery or the synthesis of a suitable semipermeable membrane. Such a membrane must: a) be semipermeable with respect to an ionic solution; b) resist chemical reaction with the solution; and c) possess a physical structure which permits a reasonable rate of water diffusion.

Breton (2) investigated the semipermeability of films prepared from a variety of polymers and concluded that, among those tried, cellulose acetate film possessed the most desirable features as a semipermeable membrane for sodium chloride solutions. Ninety-six percent of the ions were rejected from solutions ranging in concentration from 0.1 to 0.6 molar. Nevertheless, cellulose acetate could not conceivably be used in an economic application of Reid's process. The effluent flow rate was of the order of 25 ul. per hour per cm.^{2} of film, one-half mil thick, in contact with 0.1 molar sodium chloride under a pressure of 600 psi. Furthermore, the permselectivity of the film failed after six to fourteen days. This failure was shown by Kuppers (3) to be associated with the hydrolysis of acetyl groups from the polymer chains.

Although cellulose acetate was not suited to practical application of osmotic desalting of saline waters, it did offer a means of studying the mechanism by which water is selectively transported across such membranes. It was hoped that this mechanism could be elucidated to the extent that a more practical membrane could be synthesized. Hence, Breton (2) initiated an investigation from which stemmed the following theory.

"Those ions and molecules that cannot enter into hydrogen bonding with the membrane are transferred by hole-type diffusion. The rate of diffusion appears to be governed by a water-cellulose acetate structure. The reaction between water and the cellulose acetate polymers to form bound water regions is induced by compressing the membrane. As pressure is applied on the membrane, more bound water is produced which causes the rate of hole-type diffusion to decrease."

"On the other hand, those ions and molecules that can associate with the membrane through hydrogen bonding actually combine with the membrane and are transported through it by allignment-type diffusion. The formation of the water-cellulose acetate structure does not appreciably diminish the diffusion rate of water through the membrane."

This theory was supported by experimental work showing that: a) salt rejection of cellulose acetate film was relatively poor at low pressures, increased rapidly in the interval of 150 to 250 psi, then approached 100 percent asymptotically with further increase in pressure; b) the dielectric constant of moist film increased more rapidly under compression than that of dry film; c) semipermeability was correlated with electrical resistance of these membranes to passage of ions capable of forming hydrogen bonds, but not of ions which may participate in hydrogen bonding; and d) transference numbers of sodium and chloride ions were such that semipermeability could not be attributed to an ion exchange reaction with the membrane, comparable to that described by McKelvey et al. (4).

The magnitude and sign of the activation entropy, according to the Absolute Reaction Rate theory (5), will depend upon the relative order associated with the reactant and the activated state. An increase in order in passing from the reactant state to the activated state will be indicated by negative activation entropy. If we now apply the Absolute Reaction Rate theory to the diffusion of water across a cellulose acetate film, the liquid water on the side of the membrane maintained at the higher pressure will be the reactant and the water-cellulose acetate structure will be the activated state. A simple hole-type diffusion, involving no disruption of the membrane, should have zero activation entropy. On the other hand, alignment-type diffusion, involving hydrogen bonding, would imply a rather highly ordered activated state, and hence, a negative activation entropy. Therefore, if Breton's theory is essentially correct, it should be possible to observe a negative activation entropy for the diffusion of water through cellulose acetate films. Furthermore, a change in the mechanism of water transport across the membrane at higher pressure might be reflected in activation entropy values.

It is also reasonable to expect that water incorporated into the polymer structure would alter its mechanical properties in direct proportion to the strength of bonding forces involved.

The purpose, then, of the study described in this dissertation was: a) to determine diffusion coefficients and activation entropies for the diffusion of various liquids and gases through cellulose acetate and other polymer films under high pressure differentials; b) to study the compressive deformation and elastic properties of moist and dry cellulose acetate film; and c) to interpret these findings in the light of Breton's theory regarding the mechanism of water and ion flow through cellulose acetate membranes.

CHAPTER I

DIFFUSION COEFFICIENTS AND ACTIVATION ENTROPIES

1.1 Apparatus

The essential elements of the apparatus (Fig. 1) used for these measurements were: a) a film support of porous stainless steel inserted in monel metal blocks; b) a fluid reservoir tank; c) a cylinder of nitrogen gas, the compressant; and d) a flow meter (dilatometer) connected to the side of the film maintained at atmospheric pressure. The film support and fluid reservoir were immersed in a constant temperature water bath in which the temperature was controlled to within 0.05 degrees K.

1.2 Procedure

The flow rate of the fluid diffusing through the film was measured over a temperature range of 290 to 330 degrees K. and pressure differentials from 250 to 1000 psi. If for a particular pressure differential a straight line, with no perceptible inflection, was obtained from a plot of log rate versus reciprocal temperature, it was assumed that an activated rate process involving but one rate determining step was being observed. With this condition satisfied,

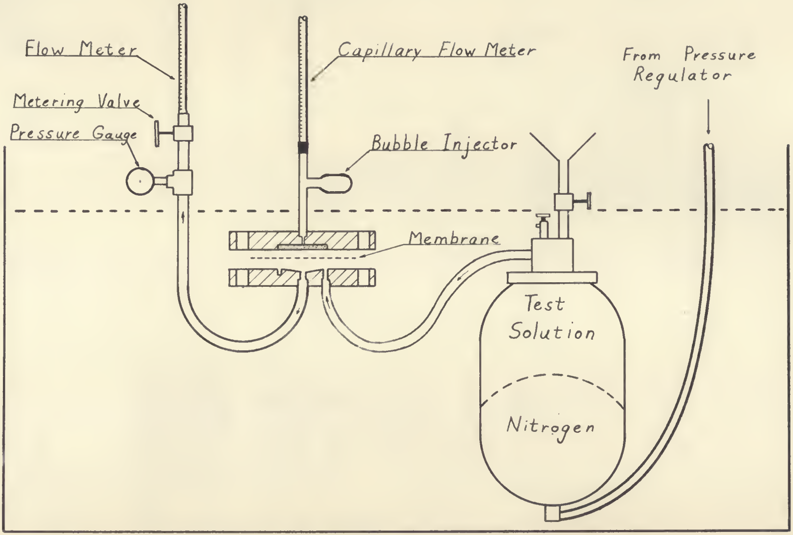


Fig. 1 .--Expanded view of apparatus used for kinetic studies.

the experimental activation energy, E_a, was taken from the slope of this line in accordance with the formula:

$$\log \text{rate} = \frac{-E_a}{2.303\ R}\ \frac{1}{T} + C.$$

The slope was calculated as a statistical regression coefficient from sets of 12 to 20 rate measurements.

The diffusion coefficient, defined as the rate of material transfer across a unit surface per unit concentration gradient, was obtained by assuming that measured flow rate was the resultant of two opposing rates, each having the same rate constant, k, and each proportional to the activity, α, of the diffusing fluid. Hence:

$$\text{Rate} = k(\alpha - \alpha_o)$$

where α is the activity of the fluid on the high pressure side of the film and α_o that on the side of the film exposed to atmospheric pressure. The activity, α, of the liquid was determined from the thermodynamic relation:

$$\Delta G = RT \ln \frac{\alpha}{\alpha_o} = \int_{P_o}^{P} V dP$$

where V, the molar volume of the liquid equals the molar volume at 273 degrees Kelvin multiplied by the ratio: $\frac{\rho_{273}}{\rho_T}$

where ρ is density. Neglect of water compressibility resulted in an error in molar volume of less than 0.5 percent (6). Hence,

$$\ln \alpha = V_{273} \frac{\rho_{273}}{\rho_T} \frac{P - P_o}{RT} .$$

If we assume the activity gradient to be linear, the film thickness multiplied by the specific rate constant, k, gives the experimental diffusion coefficient, D, which has the dimension of cm.^{2}/sec.

General definitions of diffusion velocities and the Absolute Reaction Rate theory (5) make possible a theoretical formulation of the diffusion coefficient, D, (see Appendix),

$$D = e \lambda^2 \frac{\bar{k} T}{h} e^{\Delta S^*/R} e^{-E_a/RT} ,$$

in which the entropy of activation, ΔS^*, and the mean free path, λ, are the only unknown quantities. Hence, if we assume a value for λ and use the experimentally determined D, we may calculate ΔS^*. The mean free path is the distance a molecule moves from one equilibrium position to the next and must be of the order of magnitude of the effective diameter of water molecules. A 50 percent error in the estimation of λ would change the absolute value of the activation entropy by approximately 1.5 cal./mole-degree. We shall take λ equal to 10^{-7} cm. which is the value assumed by Levi (7) for the diffusion of water vapor through cellulose acetate.

Attention is called to the tacit assumption that the diffusing molecule encountered a homogeneous membrane barrier. If, however, there existed in the film crystalline regions whose dimensions were large relative to that of the diffusing molecule, the area of the film through which diffusion could have occurred would have been reduced, and we thus would have observed a rate process involving a fraction of the total film surface. Let us suppose this phenomenon prevailed and that but half of the film area was permeable. The effect thereof would have been to increase activation entropy valuesby 4.35 (log 2) = 1.3 cal./mole-degree. The difference would not have altered the interpretations made of activation entropy values, the most significant of which depended upon relative rather than absolute values.

Since rate measurements were made on a steady-state process, calculations were simpler than they otherwise would have been. A sample calculation can be seen in the Appendix.

1.3 Results

Preliminary trials with cellulose acetate film gave hysteresis curves which clearly indicated a need for an induction period at high pressure to produce a stable state of the polymer which would give reproducible flow rates. There was no further indication of hysteresis effects following an induction period of 24 hours at 750 or 1000 psi and 320 degrees K.

Diffusion coefficients, activation energies, and activation entropies for the diffusion of water through two different thicknesses of cellulose acetate film at several pressure differentials are given in Table 1. Corresponding data for a cellophane film are contained in Table 2.

Very erratic flow rates were obtained for the diffusion of water through non-irradiated polyethylene (0.8-1.0 mil DYNK-1) film supplied by the Bakelite Company, and Nylon (1.0 mil "Zytel" 42X) film supplied by the du Pont Company. Activation energies were unattainable. The diffusion of water through irradiated polyethylene (1.5 mil "Alathon" 10) and "Teflon" (2 mil) films supplied by the du Pont Company was less than could be measured in our apparatus, i.e. the diffusion coefficient was less than 10^{-11} cm.^{2}/sec.

Reliable data for the diffusion of methanol through cellulose acetate resulted only at pressure differentials of 750 and 1000 psi (Table 3).

An attempt was also made to obtain activation entropies for the diffusion of nitrogen gas through cellulose acetate and cellophane. For a 0.33 mil film of cellulose acetate (40% acetyl) the diffusion coefficient at 500 psi was approximately 8.8 X 10^{-7} cm.^{2}/sec. and was essentially temperature independent, while that through 0.88 mil cellophane was less than 7 X 10^{-12} cm.^{2}/sec. at 750 psi. Reliable activation energies, and hence entropies, could not be extracted from this data.

Table 1. Diffusion of water through cellulose acetate (40% acetyl) films cast from acetone solution.

Film Thickness 0.33 mils

Pressure psi.	Diffusion Coefficient at 30 deg. C. cm.^{2}/sec. X 10^8	Experimental Activation Energy cal./mole	Activation Entropy cal./mole/degree
250	14.9	5160	-12.8
500	10.0	5002	-14.0
750	8.8	4975	-14.4
850	9.5	5022	-14.1
1000			

Film Thickness 0.67 mils

Pressure psi.	Diffusion Coefficient at 30 deg. C. cm.^{2}/sec. X 10^8	Experimental Activation Energy cal./mole	Activation Entropy cal./mole/degree
250	13.2	7660	-4.7
500	11.7	4838	-14.2
750	10.2	4906	-14.3
850			
1000	9.2	6105	-10.3

Table 2. Diffusion of water through cellophane (du Pont PT-300). Film thickness 0.88 mils.

Pressure psi.	Diffusion Coefficient at 30 deg. C. cm.^{2}/sec. X 10^7	Experimental Activation Energy cal./ mole	Activation Entropy cal./mole/degree
250	16.5	4257	-10.9
500	19.0	4180	-10.9
1000	17.5	4894	-8.7

Table 3. Diffusion of methanol through cellulose acetate (40% acetyl) cast from acetone solution. Film thickness 0.67 mils.

Pressure	Diffusion Coefficient at 30 deg. C.	Experimental Activation Energy	Activation Entropy
psi.	$cm.^2/sec. \times 10^8$	cal./mole	cal./mole/degree
250	----------	unattainable	--------
500	----------	unattainable	--------
750	3.3	4712	-17.2
1000	18.3	6960	-6.4

The experimental data described thus far are summarized in Table 4. It should be emphasized that these data were obtained with film which had been stabilized at high pressure differentials. Thus, in the case of cellulose acetate, the film would have been 'induced' into the semipermeable condition described by Breton (2).

The results described below represent a study of the 'induction' process in which there is an important change in the semipermeability of cellulose acetate membranes. A film of cellulose acetate (40% acetyl) was cast from acetone solution such that its thickness was approximately 0.67 mils. Diffusion coefficients, activation energies, and activation entropies were determined, starting with a pressure differential of 50 psi, increasing in small increments to 1000 psi, and then returning stepwise to 200 psi.

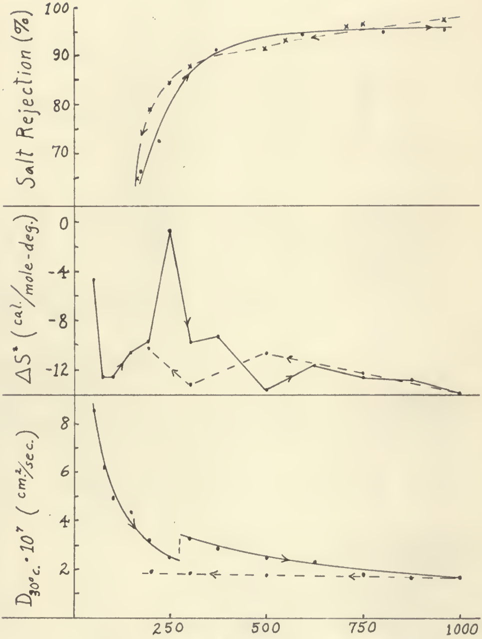
The diffusion coefficient dropped sharply with

Table 4. Diffusion coefficients, activation energies, and activation entropies for the diffusion of water, methanol, and nitrogen through several polymer films over a range of pressure differentials.

Film	Diffusant	Film thickness (mils)	Range Pressure differentials (psi)	Range of diffusion coefficients, at 30° C., D (10^{-8})	Range of activation energies, E_a (cal./mole)	Range of activation entropies, S^* (cal./mole-deg.)
Cellulose Acetate (40% acetyl)	water	0.33, 0.67	250...1000	9.2 .. 15.0	4906..7660	-4.7 .. -14.4
	methanol	0.67	750...1000	3.3 .. 18.3	4712..6960	-6.4 .. -17.2
	nitrogen	0.33	500	88	- - -	- - -
Cellophane	water	0.88	250...1000	165 .. 190	4180..4894	-8.7 .. -10.9
	nitrogen	0.88	750	less than 0.001	- - -	- - -
Polyethylene (non-irradiated)	water	1.0	1000	0.014	- - -	- - -
Polyethylene (irradiated) "Alathon" 10	water	1.5	1000	less than 0.001	- - -	- - -
"Teflon"	water	2.0	1000	less than 0.001	- - -	- - -
Nylon "Zytel" 42X	water	1.0	1000	approx. 0.1	- - -	- - -

increasing pressure (Fig. 2) up to about 250 psi where a sudden shift to a higher value occured. As the pressure differential was increased beyond 250 psi, and up to 1000 psi, the coefficient decreased asymptotically. The coefficient increased but slightly on the return sequence of decreasing pressure differentials, 1000 psi downwards.

Activation entropy values were relatively high at 50 psi and at 250 psi, the pressure differential at which the break occured in the diffusion coefficient trend. Beyond the critical point of 250 psi the general trend of entropy values was toward more negative values reaching a minimum of -13.9 cal./mole-degree at 1000 psi, and all values on the return sequence of decreasing pressure differentials were less than -10 cal./ mole-degree.



Pressure differential across film (psi)

Fig. 2 .-- Changes in the entropy of activation for diffusion and in the diffusion coefficient which occur as cellulose acetate film is 'induced' to a semipermeable condition by means of water diffusion under high pressure differentials. Salt Rejection data were taken from the work of Breton (2).

CHAPTER II

COMPRESSIVE DEFORMATION OF CELLULOSE ACETATE AND CELLOPHANE

2.1 Apparatus and Procedure

An apparatus (Fig. 3) was constructed for the purpose of measuring film deformation under compression. The base was a 10 inch I-beam, 48 inches long. A fulcrum arm, 30 inches long, was mounted such that its pivot point (one end of the arm) was 7 inches above the midpoint of the upper surface of the base. Weights were suspended from the other end of the arm. The fulcrum arm, in a horizontal position, was allowed to bear on matched steel cylinders, 1.5 inches in diameter, placed such that their axis was 3 inches from the pivot point of the fulcrum arm. The film to be compressed was placed between polished, optically flat, end surfaces of the steel cylinders. A light weight aluminum-alloy fork (extending in the direction opposite to that of the fulcrum arm) was mounted with bearing points on two lugs set in either side of the upper cylinder, and on a knife edge placed 1.25 inches from the axis of the cylinders. A dial gauge, calibrated in units of 10^{-4} inches was firmly supported from the base so as to make contact with the

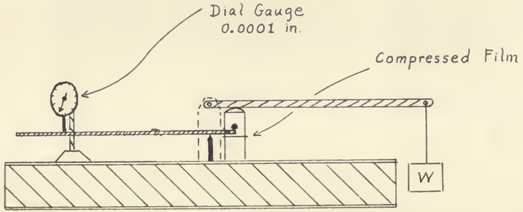


Fig. 3 .--Apparatus for measuring compressive deformation of thin films.

aluminum fork. This fork magnified the displacement along the axis of the cylinders 11.47 fold. The elastic deformation of the apparatus itself (the correction subtracted from readings) was 8.4 (10^{-4}) inches on the cylinder axis per 1000 psi applied to cylinder end surfaces. The sensitivity of the apparatus was 8.7 (10^{-6}) inches and the reproducibility of a single measurement was approximately ± 8.7 (10^{-6}) inches. Displacements, normal to the surface, of film layers about 2 (10^{-3}) inches thick were measured. Therefore, the expected error of a single measurement, expressed as percent change in dimension, was approximately 0.43 percent. However, it seemed wise to double this figure because an error of this magnitude also could have occurred in the calibration of the apparatus. Hence, it was considered that the expected error of reported values was less than one percent of the film thickness. The measurements reported are those which were taken, at a particular pressure, after time had been allowed for elastic 'creep' (8) or for stress relaxation to occur if such were manifest.

2.2 Results

Cellulose acetate (40% acetyl) film cast from acetone solution was elastically deformed by approximately 13 percent of its thickness at a pressure of 1000 psi (Table 5). When the film was saturated with water, the elastic deformation was less than 3 percent of the thickness. Repeated cycles of compression and relaxation of cellulose acetate film in contact with excess moisture resulted in progressively greater film swelling and decreased compressive deformation up to, what appeared to be, the saturation point (Tables 5,6).

In contrast, dry cellophane (du Pont PT-300) showed elastic deformation of less than 3 percent of the thickness, while wet cellophane was deformed *plastically* more than 70 percent of the dry film thickness. Plastic flow under compression did not occur when cellulose polymer chains were cross-linked with cupric ions. The copper-cellophane complex was formed by mercerizing cellophane in 15 percent sodium hydroxide solution and then rinsing with a 5 percent solution of cupric acetate. The *elastic* deformation of wet films of 'copper-cellophane' was not much greater than that of cellulose acetate (Tables 5,6,7).

Table 5. -- Compressive deformation of cellulose acetate (3 layers of 0.67 mil film) expressed as percent of original thickness of dry film.

Pressure	DRY FILM			WET FILM (in contact with excess moisture)							
(psi)	1st cycle	2nd --		1st --	2nd --	3rd --	4th --	5th --	6th --	7th --	8th --
24	0.0	1.3	Deformed -5.2% while sorbing water under compression of 24 psi.	-5.2	-10.0	-11.8	-13.9	-15.7	-17.9	-21.4	-21.4
293	8.7			-5.2		-12.2	-13.9				
499	10.9			-5.2		-12.6	-13.9				
753	11.8			-3.0		-13.1	-15.7				
999	13.1	13.4		-1.3	- 6.5	-10.5	-14.4	-16.6	-18.3	-19.6	-19.6
753	11.9			-3.0	- 7.8	-13.1					
499	8.3			-6.5	-10.5	-14.4					
293	6.5			-7.8	-10.0	-13.5					
24	1.3	0.0		-10.0	-11.8	-13.9	-15.7	-17.9	-21.4	-21.4	-21.4

Note: Since the values recorded in the table represent percent compression, negative values will correspond to a dimension greater than that of the dry film compressed at 24 psi.

Table 6. -- Compressive deformation of cellulose acetate (3 layers of 1 mil film) expressed as percent of thickness of premoistened film.

Pressure (psi)	WET FILM (in contact with excess moisture						
	1st cycle	2nd --	3rd --	4th --	5th --	6th --	7th --
24	0.0	0.6	0.3	-2.0	-2.6	-2.6	-2.9
293	3.8	1.7	0.3	-1.2	-2.0		
499	6.6	3.8	1.5	-0.9	-2.0	-2.0	-2.0
753	7.0	3.8	2.0	-0.3	-0.6		
999	9.0	4.1	2.0	-0.6	-0.6	-0.6	-1.2
753					-0.9		
499	5.8	2.9		-0.3	-0.9		-2.6
293	4.4	1.5		-1.2	-1.7		
24	0.6	0.3	-2.0	-2.6	-2.6	-2.9	-2.6

Note: Since the values recorded in the table represent percent compression, negative values will correspond to a dimension greater than that of premoistened film compressed at 24 psi.

Table 7. -- Compressive deformation of copper-cellophane complex (2 layers of 1.0 mil film) expressed as percent of original thickness of dry film.

Pressure (psi)	DRY FILM 1st cycle	2nd --	3rd --		WET FILM (in contact with excess moisture) 1st --	2nd --	3rd --	4th --
24	0.0	0.0	-0.4	Deformed -7.4% while sorbing water under compression of 24 psi.	-7.4	-6.1	-3.5	-3.5
499					1.3			
999	4.8	4.8	5.2		---	0.0	0.0	0.0
499					---			
24	0.0	-0.4	0.0		-6.1	-3.5	-3.5	-3.5

CHAPTER III

INTERPRETATION OF EXPERIMENTAL RESULTS

3.1 Activation Entropy of Diffusion

Activation entropy values of -14 cal./mole-degree for the diffusion of water at 1000 psi through cellulose acetate illustrate that the water molecule is constrained to a state of high order as it is transported across the membrane. That this order is greater under high pressure differentials is indicated by an activation entropy value of -9 cal./mole-degree determined by Levi (7) for the diffusion of water vapor across cellulose acetate film under zero (total) pressure differential. Values for two different thicknesses of cellulose acetate film were in good agreement at 500 psi and above. However, at 250 psi the thinner of the two films had decidedly the lower activation entropy. This difference was attributed to the greater ease with which the thinner film underwent polymer reorientation. This reorientation will be discussed in Section 3.2.

The mechanism for the transport of water across cellophane film under high pressure differentials may be comparable to that for cellulose acetate film as indicated by activation entropy values as low as -12 cal./mole-degree.

It is not surprising that the value for cellophane is less negative than that for cellulose acetate since the latter film has a much higher crystallinity, less Brownian movement of polymer chains, and hence less chance for random diffusion to occur.

The activation entropy for the diffusion of methanol through cellulose acetate was even less than that for water. Methanol, although capable of hydrogen bonding, does not possess the capacity to form a single molecule bridge between polymer chains as might water. If bridging (cross-linking) occurred, the corresponding increase in the order of the polymer-diffusant system, beyond that of single attachment of a diffusing molecule via one hydrogen bond, would be expected to lower, still further, the activation entropy. Hence, the low activation entropy for the diffusion of methanol through cellulose acetate film does not support the theory that polymer chains of cellulose acetate are actually cross-linked by hydrogen bonded water.

3.2 The 'Induction' of Cellulose Acetate Film to a Semipermeable Condition.

It will be recalled that cellulose acetate film was not an effective semipermeable membrane for ionic solutions unless it was subjected to high pressures. The semipermeability of the membrane increased rapidly as the pressure differential across the membrane was increased to about 250 psi, then approached asymptotically the behavior of an ideal semipermeable membrane. The interval in which the diffusion coefficient and the activation entropy values were erratic corresponds to an interval of pressure differentials, 150 to 250 psi, in which the semipermeability of the film was most sensitive to pressure change (Figure 2). It is supposed that, during this 'induction' of the film to a semipermeable condition, a significant reorientation of the polymer occurred and that it was a structural change not easily reversed, as shown by the narrow range of values for diffusion coefficients and activation entropies for the decreasing sequence of pressure differentials. Breton (2) suggested that film compression would not be expected to reduce appreciably alignment-type diffusion of water. Nevertheless the diffusion coefficient for water decreased rapidly in the pressure interval corresponding to film 'induction'. A possible explanation of this decrease is that at lower pressures the water diffusion is by hole-type as well as alignment-type mechanisms, and that the hole-type diffusion is blocked as the film is compressed under higher pressures.

3.3 Compressive Deformation of Films

That wet cellulose acetate film is less deformable under compression than dry film (Table 5) has two implications. First, it adds weight to the interpretation of

Breton's dielectric constant measurements (2) on wet and dry film. Specifically, if these measurements were corrected for film deformation up to 1000 psi compression, the differences between the wet and the dry film would be even greater than reported originally. This difference in dielectric constants was presented as evidence for the presence of hydrogen-bonded water molecules in the amorphous regions of the film. Secondly, the greater mechanical strength of wet film demonstrates a strong bond between polymer chains and water in the cellulose acetate-water structure.

Successive compression and relaxation of cellulose acetate film in contact with excess moisture (Tables 5,6.) has demonstrated that compression increases the capacity of the film for bound water. This was predicted by Breton (2) from more theoretical considerations.

Although the diffusion coefficient, under high pressure differentials, for water in cellophane is roughly 10-fold greater than in cellulose acetate, nitrogen gas flows quite freely through the latter, while cellophane is nearly impermeable to the gas under similar conditions. Since the deformation of cellophane under a pressure of 1000 psi is less than 3 percent of the film thickness, film compaction cannot explain the impermeability of cellophane to nitrogen. It appears that the structure of dry cellophane is sufficiently dense that a polar molecule is required to separate the polymer chains to the extent that appreciable diffusion can occur. Obviously, amorphous regions of cellulose acetate are of a more open structure than cellophane. Nevertheless, the crystalline regions of cellulose acetate prevent the plastic flow of wet film which is observed with wet cellophane.

3.4 Semipermeability of Cellophane

In view of the known properties of cellophane, in particular its capacity to support hydrogen bonding and its high permeability to water, one may ask what can be done to make this film a more effective semipermeable membrane for ionic solutions. A consideration of work reported herein and related investigations carried out in this laboratory suggest a partial solution. One defect of cellophane seems to be excessive Brownian motion of polymer chains when wetted and concurrent plastic flow under compression. Two observations (9) strongly support this contention: a) An increase in pressure differential across the film from 600 to 1500 psi raised the salt rejection from 8 to 12 percent. It is reasonable to expect that higher pressures would restrict, to some degree, Brownian motion and hence random diffusion. b) When cellulose polymer chains were cross-linked with cupric ion the salt rejection was increased to 18 percent at 600 psi. Moreover, plastic flow, characteristic of wet cellophane compressed at 1000 psi, did not occur. Hence, it appears that cross-linking elements might be incorporated into cellophane in such a manner that an optimum spacing of polymer chains and sufficient constraint of Brownian motion would result in an efficient semipermeable membrane for ionic solutions. An important drawback to such a modification of the cellulose structure is that it is apt to reduce significantly the favorable diffusion coefficient of water through cellophane.

CHAPTER IV

SUMMARY

The mechanism of water transport across cellulosic films under high pressure differentials was studied in an attempt to explain the semipermeability of these films when used as osmotic membranes for ionic solutions.

Diffusion coefficients and activation entropy values for the diffusion of water and other fluids across various polymer films were determined, and compressive deformation of cellulose acetate and cellophane films was measured.

Activation entropy values for the diffusion of water across both cellulose acetate and cellophane films illustrated that the water molecule is constrained to a state of high order as it is transported across the membrane under high pressure differentials, the greater order being associated with cellulose acetate films. Activation entropy values for the diffusion of methanol across cellulose acetate film failed to support the proposition that polymer chains are actually cross-linked by hydrogen bonded water. It appears more likely that but one hydrogen of the water molecule participates in hydrogen bonding. The possibility of additional order due to dipole alignment is not excluded.

A significant reorientation of the polymer, in the pressure interval in which cellulose acetate film is 'induced' into a semipermeable condition, was indicated by pressure dependent fluctuations of diffusion coefficients and activation entropies in this interval.

The greater mechanical strength of wet cellulose acetate film under a compressive force, applied normal to the surface, demonstrated a strong bond between polymer chains and water in the cellulose acetate-water structure. Compression also increased the capacity of the film for bound water.

Wet cellophane film deformed plastically under compression. Cross-linking polymer chains of cellophane film prevented plastic flow and, at the same time, increased the semipermeability of the film for sodium chloride solutions.

APPENDIX

Application of the Absolute Reaction Rate Theory to Diffusion.

Sample calculation of diffusion coefficient and entropy of activation.

APPLICATION OF THE ABSOLUTE REACTION RATE THEORY TO DIFFUSION (5)

(a) The number of molecules per second, V_f, moving in a forward direction through a cross-section of 1 cm.^{2} = $Nc\lambda k$.

Where:

c = moles per cm.^{3} of diffusing molecules.

λ = distance between successive equilibrium positions.

N = Avogadro's number.

k = specific rate constant for diffusion.

(b) The number of molecules per second, V_r, moving in the reverse direction through same cross-section = $N(c + \lambda \frac{dc}{dx}) \lambda k$.

Where: $\frac{dc}{dx}$ = concentration gradient.

(c) Resultant Flow: $V = -N\lambda^2 k \frac{dc}{dx}$.

(d) But by Fick's Law: $V = \frac{\frac{ds}{dt}}{A} = -ND \frac{dc}{dx}$.

Where: A = the cross-sectional area in cm.^{2}

D = the diffusion coefficient.

(e) Combining (c) and (d): $D = \lambda^2 k$.

(f) By the Absolute Reaction Rate theory for a unimolecular process, $k = \frac{\bar{k}T}{h} K^* = e\,\frac{\bar{k}T}{h}\, e^{-E_a/RT}\, e^{\Delta S^*/R}$.

Where: $\bar{k}$ = Boltzmann's Constant

h = Planck's Constant

T = Absolute Temperature

E_a = Experimental Activation Energy

ΔS^* = Activation Entropy

R = Gas constant

(g) Hence, combining (e) and (f),

$$D = e\,\lambda^2\, \frac{\bar{k}T}{h}\, e^{-E_a/RT}\, e^{\Delta S^*/R}.$$

SAMPLE CALCULATION OF DIFFUSION COEFFICIENT AND ENTROPY OF ACTIVATION

The following data were recorded with a pressure differential of 50 psi using a film 0.67 mils thick.

X 1/T (10^3) (T = degrees K.)	Y $\log_{10}$ Rate (Rate = μl./hr./cm.^{2})
3.138	0.928
	0.923
	0.916
3.227	0.733
	0.728
	0.721
3.320	0.506
	0.528
	0.592
3.442	0.493
	0.485
	0.484

(a) Determine equation of straight line of best fit relating Y to X, using statistical notation of Snedecor (10).

$N = 12$

$SX = 39.381$

$SY = 8.037$

$\bar{X} = 3.282$

$\bar{Y} = 0.670$

$SX^2 = 129.391011$

$(SX)^2/N = 129.238597$

$Sx^2 = 0.152414$

$SXY = 26.154684$

$(SX)(SY)/N = 26.375425$

$Sxy = -0.220741$

Slope = $\frac{Sxy}{Sx^2}$ = -1.4483 units of Y per unit of X

= -1448.3 units of 1/T per unit of X.

(b) Obtain activation energy from the slope determined in (a).

$$\log \text{rate} = \frac{-E_a}{2.303\ R} \ \frac{1}{T} + C$$

Slope of log rate versus 1/T = -1448.3 = $\frac{-E_a}{2.303\ R}$.

$$E_a = 6630 \text{ cal./mole}$$

(c) Determine diffusion coefficient at 30 degrees C. (X = 3.3).

$Y = \bar{Y} - 1.4483\ (X - \bar{X})$

$Y = 0.670 - 1.4483\ (3.3 - 3.282)$

$Y = 0.644$

antilog Y = 4.41 μl./hr./cm.^{2} = Flow rate.

Flow rate = $\frac{4.41\ (10^{-3})}{3.6\ (10^3)}$ cm.^{3}/sec./cm.^{2}

Flow rate = $1.225\ (10^{-6})$ cm./sec.

Flow rate = Specific rate constant, k, multiplied by difference in activities, $\alpha - \alpha_0$.

$$\log \alpha = V_{273} \ \frac{\rho_{273}}{\rho_T} \ \frac{P - P_0}{RT}$$

$\log \alpha = 0.0064 \ \frac{psi}{T\rho_T}$; when $1/T = 3.3(10^{-3})$,

$T\rho_T = 302.$

$$\log \alpha = 0.0064 \ \frac{50}{302} = 0.001059$$

$$\alpha = 1.00244$$

$$\alpha - \alpha_0 = 0.00244$$

$$k = \frac{\text{flow rate}}{\alpha - \alpha_0}$$

$k = 5.02\ (10^{-4})$ cm./sec.

D = k multiplied by film thickness.

$D = 1.688\ (10^{-3})\ 5.02\ (10^{-4})$.

$D = 8.543\ (10^{-7})$ cm.^{2}/sec.

(d) Use Eyring's Equation to determine activation entropy.

$$D = e\lambda^2 \frac{\bar{k}T}{h} e^{\Delta S^*/R} e^{-E_a/RT}$$

$$\log D = \log\left[e\lambda^2 \frac{\bar{k}T}{h}\right] + \Delta S^*/2.303\ R - E_a/2.303\ RT.$$

$$-6.0685 = -0.331 + \frac{\Delta S^*}{4.58} - 4.780$$

$\Delta S^* = -4.39$ cal./mole-degree.

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BIOGRAPHICAL NOTES

James Richard Kuppers was born in Newland, Indiana, August 4, 1920. He attended elementary and high schools in Vero Beach, Florida, and enrolled in the University of Florida in 1938. A portion of the year 1941 was spent in Port St. Joe, Florida, as an employee of the St. Joe Paper Company. He received the B. S. degree from the University of Florida in 1943. His tour of active duty with the Amphibious Force of the U. S. Navy extended from June 1943 to February 1946. He enrolled in the Graduate School of Louisiana State University in February 1946 and was granted a M. S. degree by that institution in August 1947. While employed by the Research Department of the United Fruit Company from 1947 to 1954, he resided in the Republics of Panama, Costa Rica, and Honduras. Since his return to the University of Florida in September 1954, he has been employed as a teaching assistant and subsequently as a research assistant with the Saline Water Project, sponsored by the Office of Saline Water, U. S. Department of the Interior. He is a member of Sigma Xi, the American Chemical Society, and the American Association for the Advancement of Science.

This dissertation was prepared under the direction of the chairman of the candidates supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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